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EFFECT OF TECHNOLOGICAL PARAMETERS ON THE PROPERTIES OF CuO – TiO_2 SOL – GEL FILMS

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The effect of technological parameters on the properties of 2- and 42-day film-forming solutions of the system CuO – TiO_2 is analyzed. It is found that the initial components have a strong effect on the maturing of film-forming colloidal solutions (FCS) and the properties of coatings. The properties of coatings obtained from solutions of different age are associated with changes in their microstructure. The index of refraction and the thickness of the films from 42-day FCS are essentially independent of the calcination regime; the variation of the refractive coefficient and chemical stability is inconsistent.

It is well-known [1] that thin sol – gel film coatings are nearly glassy so that their properties, just as the properties of glass, should depend on the thermal history — the heat-treatment regime.

The film-forming colloidal solutions (FCS) in the form of sols in sol-gel technology age during storage and use. The state of the dispersed phase changes, which should be reflected in the properties of FCS and coatings. In conventional glassmaking, if measures are taken to prevent the separation and contamination of the mixture of raw materials, the mixture can be stored for quite a long time, and the properties of the glass obtained will be constant to within the limits of the experimental error.

The objective of the present work is to study the relationship between the age of FCS, the past history of the coating, and the properties of sols and films.

Five compositions belonging to the two-component system CuO – TiO_2 differing by the ratio of the film-forming oxides or the raw materials used for preparing the FCS were studied. Copper oxide was introduced in the solution as copper chloride or copper nitrate, TiO_2 was introduced by alkoxides: tetraethoxytitanate $Ti(OC_2H_5)_4$ (TET) or tetrabutoxytitanate $Ti(OC_4H_9)_4$ (TBT). Hydrochloric or nitric acid (if the copper oxide was introduced as a chloride or nitrate, respectively) served as the catalyst for the hydrolysis of alkoxides and ethyl alcohol served as the solvent. The total mass content of the film-forming oxides in all solutions (the FCS concentration) was the same and equal to 5%. The aging time of sols was 2 and 42 days.

The capillary method was used to measure the viscosity of FCS (VPZh-1 viscosimeter). Samples of heat-polished sheet glass (70 × 70 × 5 mm) were immersed in a solution and extracted at a constant rate 1 mm/sec, held for 2 – 3 h in air at room temperature to complete the hydrolysis and polycondensation processes, and calcined in a furnace with Silit heaters at temperatures 350, 450, or 550°C for 30 min. All measurements were performed on the side of the glass which during production was in contact with the protective gas atmosphere of the furnace.

The structural changes in the films were studied using photomicrographs obtained with magnification × 100 (MIM-8M light microscope). The index of refraction n, the thickness h (LÉF-ZM-1 ellipsometer), and the coefficient of mirror reflection R (Pul’sar spectrocolorimeter) were measured. The chemical stability T was estimated according to the change in the thickness of the coating after etching in water (30 days) or a 0.1 N NCl (30 min). According to the procedure adopted, the lower the value of T, the higher chemical stability will be.

All experiments and measurements were performed repeatedly, and the results were analyzed statistically. The structural-phase transformations occurring with a change in the composition or age of FCS were studied by means of DTA and XPA of powders obtained by evaporating the corresponding solutions.

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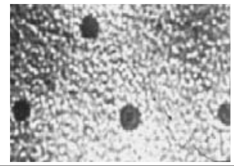
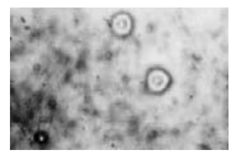
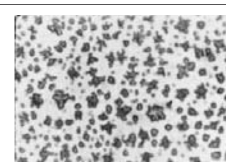
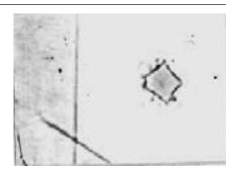
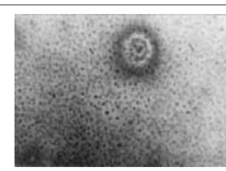
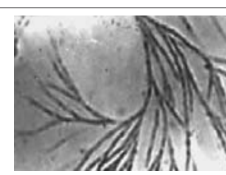
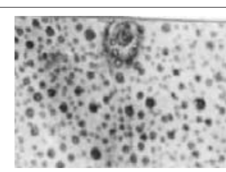
TABLE 1.

Composition No.	Molar content in film, % (introduction into FCS)		FCS properties			Photomicrograph of coatings calcined at 450°C
	CuO	TiO_2	age, days	viscosity, mm^2/sec	precipitate presence	
1	15 (by copper chloride)	85 (TBT)	2	3.21	Absent	
			42	3.01	Present, large quantity	No data
2	30 (by copper chloride)	70 (TBT)	2	2.92	Absent	
			42	2.70	Present, but less than in composition No. 1	
3	45 (by copper chloride)	55 (TBT)	2	2.74	Absent	
			42	1.84	Little quantity	
4	30 (by copper nitrate)	70 (TBT)	2	2.87	Absent	
			42	2.67	″	
5	30 (by copper chloride)	70 (TET)	2	2.96	″	
			42	2.65	Present, large quantity	

The molar content of titanium and copper oxides in the films, the form of the initial raw material, the viscosity of FCS with different age, and photomicrographs of the coatings calcined at 450°C are presented in Table 1.

There are no residues in the 2-day sols. The factors which relate the viscosity with the form of the raw material used and the characteristics of the variation of the microstructure of the coatings are examined in [2]. After 42 days of storage precipitates formed in all FCS except for composition No. 4. Visually, their number decreases with the TiO_2 content in compositions Nos. 1 – 3 as well as when TET is replaced with TBT (compositions Nos. 2 and 5) and copper chloride with copper nitrate (compositions Nos. 2 and 4). The viscosity of the 42-day FCS decreases by 6 – 10%; the largest effect is observed in copper chloride enriched FCS No. 3, where it decreased by 33%. The microstructure changes radically. In all coatings, the dendritic inclusions vanish and this is accompanied by vanishing of the crystalline phase $CuCl_2 \cdot 2H_2O$ in powders heat-treated up to 800°C (Table 2). The results of XPA attest to chemical reactions occurring between the film-forming oxides, resulting in the formation of the solid solution $(Ti_{1-x}Cu_x)O_2$ in all powders from the 42-day FCS. The transformations observed are confirmed by thermograms (see Fig. 1), where a shift and change of the magnitude of the exo- and endothermal effects in the same powders of different age are observed.

The 30-min calcination temperature and some properties of coatings obtained from 42-day FCS are presented in Table 3.

The coatings heat-treated at a fixed temperature can be arranged in the following order according to the change in the confidence intervals of the distribution of the values of n, R, h, T_{H_2O} and T_{HCl} (the numbers represent the number of a composition):

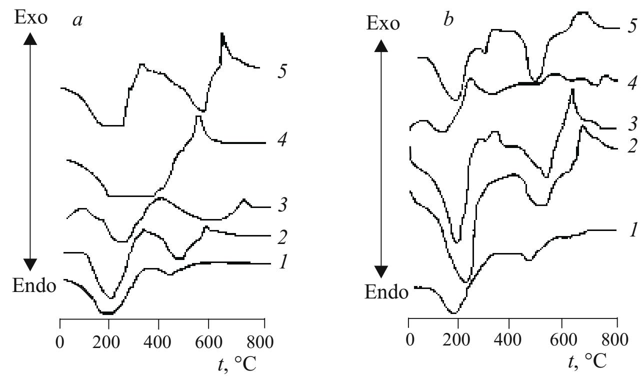


Fig. 1. Thermograms of powders obtained from 2-day (a) and 42-day (b) FCS (see Table 1). The numbers on the curves correspond to the composition numbers.

350°C n: 1 = 2, 2 > 5, 2 > 4;
R: total 1, 2 > 3, 2 > 5, 2 > 4;
h: 1 = 2, 4 > 2, 2 > 5;
T_{H_2O}: 2 > 1;
T_{HCl}: 1 = 2, 4 > 2, 5 = 2;

450°C n: 1, 2 > 3, 2 > 4, 2 > 5;
R: 1 > 2 > 3, 2 > 4, 2 = 5;
h: 1 = 2 = 3, 4 = 2, 2 > 5;
T_{H_2O}: no data;
T_{HCl}: 2 = 3, 2 = 5;

550°C n: 1 > 2 > 3, 2 > 5, 2 > 4;
R: 1, 2 > 3, 2 > 5, 2 > 4;
h: 1 = 2 = 3, 2 = 4, 2 = 5;
T_{H_2O}: 1 = 2 = 3, 2 > 4, 2 = 5;
T_{HCl}: 1 = 2 = 3, in particular 1 > 3, 2 = 5.

TABLE 2.

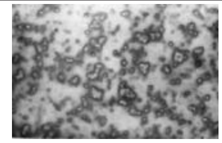
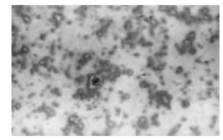
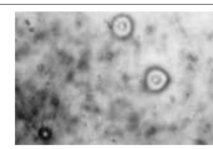
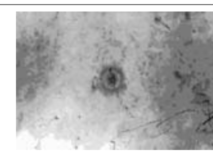
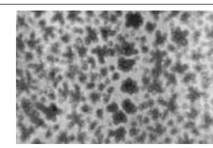
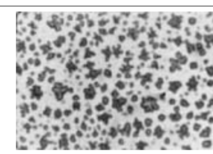
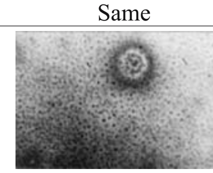
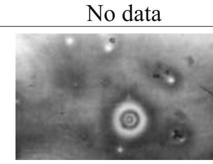
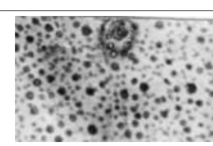
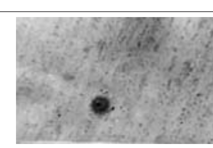
Composition No.	Molar content in film, % (introduction into FCS)		Results* of XPA of powders obtained form FCS			
			2-day		42-day	
	CuO	TiO_2	initial	heated to 800°C	initial	heated to 800°C
1	15 (by copper chloride)	85 (TBT)	73 TiO_2** 33 $CuCl_2 \cdot 2H_2O$	240 TiO_2***	100 TiO_2** 20 $CuCl_2 \cdot 2H_2O$	185 solid solution $(Ti_{1-x}Cu_x)O_2$
2	30 (by copper chloride)	70 (TBT)	44 TiO_2** 103 $CuCl_2 \cdot 2H_2O$	248 TiO_2*** 25 $CuCl_2 \cdot 2H_2O$	60 TiO_2** 30 $CuCl_2 \cdot 2H_2O$	165 solid solution $(Ti_{1-x}Cu_x)O_2$
3	45 (by copper chloride)	55 (TBT)	43 TiO_2** 220 $CuCl_2 \cdot 2H_2O$	185 TiO_2*** 45 $CuCl_2 \cdot 2H_2O$	28 TiO_2** 210 $CuCl_2 \cdot 2H_2O$	190 solid solution $(Ti_{1-x}Cu_x)O_2$
4	30 (by copper nitrate)	70 (TBT)	65 TiO_2** 101 $Cu_2(OH)_3NO_3$	242 TiO_2***	45 TiO_2** 101 $Cu_2(OH)_3NO_3$	140 solid solution $(Ti_{1-x}Cu_x)O_2$
5	30 (by copper chloride)	70 (TET)	36 TiO_2** 209 $Cl_2 \cdot 2H_2O$	168 TiO_2*** 150 $CuCl_2 \cdot 2H_2O$	130 TiO_2** 130 $CuCl_2 \cdot 2H_2O$	165 solid solution $Ti_{1-x}Cu_x)O_2$

* The content is indicated in arbitrary units.

** TiO_2 predominately in the form of anatase.

*** TiO_2 predominately in the form of rutile.

TABLE 3.

Composition No.	Calcination temperature, °C	Confidence intervals of the distribution of values of the film properties					Photomicrograph of coatings (× 100, FCS age: 42 days)
		n	R, %	T_{H_2O}, %	T_{HCl}, %	h, Å	
1	350	2.030 – 2.020	31.8 – 30.6	18.2 – 14.6	11.2 – 8.0	890 – 850	
	450	2.054 – 2.030	36.0 – 35.6	No data		790 – 700	No data
	550	2.168 – 1.982	33.1 – 31.9	30.2 – 0.6	57.3 – 12.3	710 – 670	
2	350	2.012 – 2.002	37.2 – 35.8	30.7 – 27.0	13.2 – 4.8	860 – 800	No data
	450	2.004 – 1.982	30.7 – 28.9	No data	14.0 – 5.0	940 – 770	
	550	1.971 – 1.947	32.2 – 29.5	39.7 – 33.5	12.5 – 6.9	920 – 620	
3	350			No data			
	450	1.925 – 1.875	26.5 – 25.3	33.9 – 22.0	10.5 – 1.2	760 – 560	
	550	1.874 – 1.835	26.9 – 23.5	40.5 – 33.5	7.6 – 1.2	610 – 490	No data
4	350	1.884 – 1.838	18.5 – 15.3	30.5 – 18.0	26.3 – 19.5	970 – 870	Same
	450	1.867 – 1.799	22.4 – 20.0	0	No data	940 – 810	
	550	1.838 – 1.778	23.1 – 21.5	0	Same	880 – 720	No data
5	350	2.007 – 1.863	26.0 – 21.4	35.9 – 27.5	19.0 – 7.0	780 – 630	
	450	1.933 – 1.905	30.7 – 27.0	15.0– 9.0	11.0 – 5.0	530 – 480	
	550	1.895 – 1.861	28.8 – 27.2	7.6 – 1.4	15.3 – 6.9	550 – 480	

It is evident that the index of refraction and the coefficient of mirror reflection of the films decrease or do not change from composition No. 1 to composition No. 3. Compared with composition No. 2, the values of these parameters for coatings Nos. 4 and 5 decrease, which can be explained by an increase of the number of inclusions in them (see Table 3) because of the different effect of the initial copper- and titanium-containing components on the aging processes in the same FCS. Analysis of the series showed that the index of refraction and the coefficient of reflection of the coatings are directly proportional to one another.

No distinct relationship was found between the thickness and composition of the coatings. The lack of experimental data makes it impossible to analyze correctly the dependence of the chemical stability of the films on their composition.

A similar analysis of the properties of coatings with a fixed composition, calcined at different temperatures, made it possible to construct the following series (the numbers refer to the temperature):

No. 1 n: 350 = 450 = 550;
R: 450, 550 > 350;
h: 350 > 450, 550;
T_{H_2O}: 550 = 350;
T_{HCl}: 550 > 350;
No. 2 n: 350, 450 > 550;
R: 350 > 450, 550;
h: 350 = 450 = 550;
T_{H_2O}: 550 > 350;
T_{HCl}: 350 = 450 = 550;
No. 3 n: 450 = 550;
R: 450 = 550;
h: 450 = 550;
T_{H_2O}: 450 = 550;
T_{HCl}: 450 = 550;
No. 4 n: 350 = 450 = 550;
R: 550 = 450 > 350;
h: 350 = 550 = 450;
T_{H_2O}: 350 > 450, 550;
T_{HCl}: no data;
No. 5 n: totally 350 = 450 = 550, in particular 450 > 550;
R: 450, 550 > 350;
h: 350 = 450 = 550;
T_{H_2O}: 550 > 350;
T_{HCl}: 350 = 450 = 550.

In 80% of the cases the index of refraction is independent of temperature. The coefficient of reflection increases in a regular manner (because of a decrease in the porosity of the films) with increasing calcinations temperature for compositions Nos. 1, 4, and 5 and is independent of this temperature for composition No. 3 and decreases for composition No. 2.

The film thickness is independent of the heat-treatment regime. To within the limits of experimental error, as the calcinations temperature increases, the chemical stability with respect to the effect of water decreases negligibly for coatings No. 2 and 5, is independent for coatings Nos. 1 and 3, and decreases for coating No. 4. The latter is explained by a decrease of the porosity of the coatings and prevention of the etching agent from penetrating into the films.

Comparing and analyzing the data obtained gave series which show that the index of refraction of the films remains constant to within the experimental temperatures and the aging times. The coefficient of reflection is more sensitive to the technological parameters: it is higher for coatings Nos. 2, 3, and 5 from 2-day FCS and lower for coating No. 4 compared with films from 42-day sols. This is explained by a change in the size, shape, and number of inclusions, associated with aging of FCS, in the coatings.

The thickness of film No. 1 from 2-day FCS is greater and of film No. 2 smaller than for 42-day sols. No differences were observed for any of the other coatings. These observations can be explained by a decrease of the content of the film-forming oxides in the solution as result of the formation of precipitates and the different degree of settling of the dispersed-phase particles during calcinations of the films.

The chemical stability of films Nos. 2 and 3 from 2-day FCS with respect to the effect of water is higher (and correspondingly T_{H_2O} is smaller) and that of film No. 4 lower than in the case where a 42-day solution is deposited. These results correlate well with the change in the coefficient of reflection: it is consistently higher for coatings which are more resistant to water, since both of these properties depend substantially on the porosity. On the one hand, its decrease promotes an increase of n [3] and is proportional to the value of R [4], which is related with it, and on the other hand it decreases the penetration of the etching agent into the coatings and weakens their damage. The same dependence is observed for the chemical resistance to acid for films No. 2 and 5 obtained from 42-day sols: for them T_{HCl} is greater and R is correspondingly lower than for a deposition of 2-day FCS:

350°C n: $1_{2=42}$,* $2_{42>2}$, $4_{2=42}$, $5_{2=42}$;
R: $1_{2=42}$, $2_{42>2}$, $4_{2=42}$, $5_{2>42}$;
T_{H_2O}: $1_{2=42}$, $2_{42>2}$, $4_{2=42}$, $5_{2=42}$;
T_{HCl}: $1_{42>2}$, $2_{42>2}$, $4_{2=42}$, $5_{2=42}$;
450°C n: $2_{2=42}$, $3_{2=42}$, $4_{42>2}$, $5_{2=42}$;
R: $2_{2>42}$, $3_{2>42}$, $4_{42>2}$, $5_{2>42}$;
T_{H_2O}: $3_{2=42}$, $5_{2=42}$;
T_{HCl}: $2_{2=42}$, $3_{2=42}$, $5_{2=42}$;
550°C n: $1_{2=42}$, $2_{2=42}$, $3_{2=42}$, $4_{2=42}$, $5_{2=42}$;
R: $1_{2=42}$, $2_{2>42}$, $3_{2>42}$, $4_{42>2}$, $5_{2>42}$;
T_{H_2O}: $3_{42>2}$, $4_{2>42}$;
T_{HCl}: $3_{42=2}$, $5_{42>2}$.

* Explanation of the notation: for example n : $1_{2=42}$ means that the refractive indices of the coatings No. 1 obtained from 2- and 42-day FCS, are the same to within the experimental error.

In summary, the viscosity of FCS changes during aging. This correlates with the transformation of the microstructure of the coatings and is confirmed by DTA and XPA data for the powders. The concentration and nature of the initial powders have a large effect on the maturing of FCS and the properties of the coatings. In films obtained from 42-day FCS, the index of refraction and thickness are essentially independent of the calcination regime, and the coefficient of reflection and chemical stability change inconsistently.

The microstructure of the films depends on the age of the solutions used.

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